

USE OF ETHANOLAMINE THIOGLYCOLLATE IN THE CONSERVATION OF PYRITIZED FOSSILS

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ABSTRACT. The neutralization and removal of decay products from pyritized fossil material with ethanolamine thioglycollate is described. Its use on a wide range of material is a significant improvement over previous techniques which, although satisfactory, were complex and hazardous to the preparator.

THE deterioration and even complete decomposition of pyritized fossils through oxidation is a common problem in collections throughout the world. Various conservation treatments have been described, e.g. Rixon (1976). Howie (1977*a*) reviewed these techniques, together with many of the hypotheses put forward to explain the decay process, and showed that pyrite breakdown is initiated in storage or exhibition environments solely by high relative humidity. Howie (1979*a, b*) also demonstrated that where specimens incorporating reactive pyrite (i.e. with a micro-crystalline structure) are exposed to relative humidities above 60 per cent, visible deterioration due to oxidation may occur within a few weeks.

The practice of protecting the surface of specimens from the air by coating with lacquer or resin is now considered ineffective as a safeguard since such coatings are permeable to both oxygen and water vapour. This can be readily observed by studying the surface of decayed, coated specimens (text-fig. 1A). The coating will usually have been ruptured by the sulphuric acid produced during oxidation, exposing earthy textured iron sulphate breakdown products beneath. Thus, it is advisable to remove as much of the coating as possible to expose the specimen surface for effective re-treatment. In some cases this may result in the specimen breaking up and care must be taken in noting where the pieces belong for reassembly after treatment. In most instances pyrite oxidation breakdown products are easy to identify on the surface of the specimen (Howie 1979*a*). In cases where the operator is unsure whether or not pyrite breakdown has occurred, a simple test with universal indicator paper moistened with distilled water and pressed against the affected area, will confirm this if the pH is less than or equal to 3.

The method described here replaces the ammonia neutralization process (Rixon 1976; Howie 1979*a*) and morpholine treatments (Rixon 1976) hitherto used in the British Museum (Natural History) and other laboratories. The substance now used, ethanolamine thioglycollate, is of comparatively low toxicity and can be safely employed where calcareous material or water soluble compounds, such as animal glue, are present.

ETHANOLAMINE THIOGLYCOLLATE

This material, originally developed for use in hair-perming preparations (see Robinson Brothers Limited, Technical Bulletin 210868 PAL) has three important characteristics that are relevant in the conservation of pyritic fossil material.

1. Ethanolamine is alkaline and in solution will react with and effectively wash out acidic pyrite oxidation products (i.e. sulphuric acid).

2. Thioglycollates will react with soluble and insoluble iron compounds (though not stable pyrite) and chelate or complex iron in solution as a violet-coloured ferrothioglycollate.

3. Ethanolamine thioglycollate is readily soluble in ethanol or propan-2-ol (isopropanol), as are the products of its reactions with those of pyrite oxidation; thus contact of specimens with reagents containing more than a small proportion of water, which may be damaging, can be avoided.

The chemistry of the formation of iron-thiol compounds has been described in detail (Leussing and Tischer 1963) and thioglycollic acid is currently used as a successful technique in the preparation of vertebrate fossils encrusted with haematite (Howie 1974). A major advantage of using ethanolamine thioglycollate is its solubility in organic solvents which, coupled with its high pH and the ready solubility of the violet coloured ferrothioglycollates in solvents, makes it an effective neutralization and dry-cleaning treatment for oxidized pyrite. Ethanolamine thioglycollate is supplied commercially as an aqueous solution containing 40 per cent thioglycollic acid. This material is an alkaline, colourless to pale pink viscous liquid, miscible in all proportions with water, ethanol or isopropanol. Despite its relatively low toxicity, precautions should be taken against the possible hazards associated with its use. The manufacturer's product safety data sheet should be consulted for full specifications, but generally its corrosive action necessitates the use of PVC gloves and goggles for eye protection. Its use should be restricted to a well ventilated area, preferably a fume cupboard.

METHOD

Actively decomposing specimens should initially be placed, together with containers and any associated labels, in an environment of 40–50 per cent relative humidity until treatment can commence. It may be necessary to use a desiccator for this purpose. Specimens should then be examined and note taken of their general condition, whether they are very friable or largely intact. If a specimen is very friable then the immersion procedure discussed below should be avoided as this may do more harm than good.

Loose breakdown products can be removed by either gentle brushing or scraping. Sturdier specimens can be cleaned using an 'Airbrasive' with sodium bicarbonate powder; however, this should be carried out carefully to avoid damaging any surviving original surface. Old coats of varnish and laquer can also often be removed by this process. Any wax-based adhesives or fillers should be removed by the application of methylene chloride soaked tissues or pads (Rixon 1976; Howie 1979a) as these can impair treatment. Where the original shell is preserved, particular care is needed to avoid damage when physical cleaning methods are used; in many such cases it is better not to carry out initial cleaning and proceed directly to ethanolamine thioglycollate treatment.

After cleaning, each specimen is completely immersed in a solution of between 2 per cent and 5 per cent ethanolamine thioglycollate in 95 per cent industrial methylated spirit, or alternatively absolute ethanol or anhydrous iso-propanol. The higher concentration is used on more oxidized material. The small quantities of water present in the final solution are not enough to endanger specimens during treatment. Glass beakers are ideal containers for immersion as one can observe both the iron complexing reactions and the general state of the specimen. The ethanolamine thioglycollate solution should cover the specimen by 5–6 cm to ensure adequate dilution of the reaction products, and ideally the specimen should not touch the side of the beaker. Each immersion should last between one and four hours depending on how badly decayed the specimen is. The clear colourless solution will turn a violet colour as neutralization and iron complexing occurs. The solution should be changed after a maximum of four hours immersion to prevent the violet coloured complex ferrothioglycollate anion from oxidizing to a brown insoluble precipitate which will coat the specimen. Treatment can be repeated if necessary, provided the specimen is 'washed' in clean dry alcohol between immersions. The specimen should be washed at least three times longer than the treatment time to ensure removal of reaction products.

Once reaction has slowed down or ceased altogether, i.e. when little or no violet ferrothioglycollate complex forms, the specimen should be given a final wash and allowed to dry in air. When the specimen has dried, the surface should be carefully examined and cleaned with the 'Airbrasive' to remove any remaining oxidation products. Alternatively, if the more persistent black coatings (which are usually mixtures of microcrystalline pyrite and iron oxides) remain, a further course of treatment using a more concentrated solution of ethanolamine thioglycollate (e.g. 10–15 per cent) may be effective. Cleaned fragments can be reassembled and glued using Butvar B76 in acetone (1:1 by volume) or other solvent-based cement.

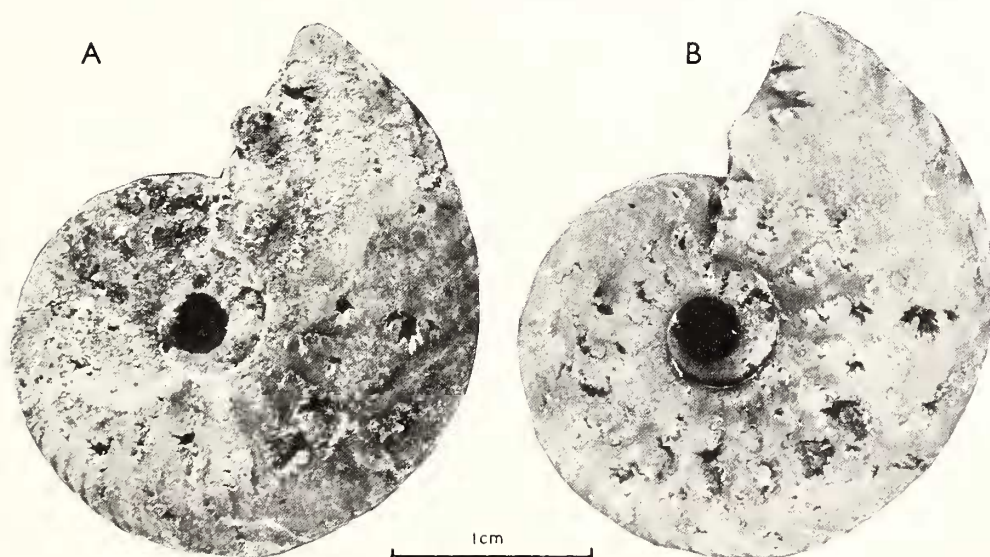
Friable and other specimens which would be damaged by immersion can be neutralized in the following manner. Place the specimen on a flat surface in a well-ventilated area and apply a paste composed of 3–5 per cent ethanolamine thioglycollate in spirit added to sepiolite in about equal portions. The area requiring treatment or the whole specimen should be covered by the paste and then by polythene or aluminium foil to prevent rapid evaporation of the solvent and left for one to three hours. Immersion of the sturdier specimens in clean alcohol is a recommended method of washing. If the specimen cannot be immersed the ferrothioglycollate complex may be removed by applications of I.M.S./sepiolite paste until clean. Consolidation of treated but friable specimens is often advisable although this will not offer protection against exposure to high relative humidity. Such consolidants as polyvinyl acetate (5–10 per cent in ethyl methyl ketone) or polyvinyl butyral (e.g. 5–10 per cent Butvar B98 dissolved in isopropyl alcohol, or 5–10 per cent Butvar B76 dissolved in acetone) are recommended. Thin coats should be applied and if more than one is necessary, adequate drying time should be allowed between each coat.

Specimen containers should be replaced where possible and labels coated or wiped clean with a tissue. Badly damaged labels can be treated by exposing to ammonia fumes or by washing in a very dilute 1 per cent ethanolamine thioglycollate solution in alcohol, and subsequently coated in a polymethyl methacrylate emulsion (Primal AC 73), or alternatively, inserted into small polythene sachets which can be pressure or heat sealed. Storage of treated material should be in a low humidity environment (40–55 per cent relative humidity), which will help prevent further decay. Howie (1979a) and Thompson (1978) described methods for controlling and modifying storage and exhibition environments using various techniques.

Conclusion

The use of ethanolamine thioglycollate in palaeontological conservation has provided a satisfactory method of treating decaying pyritized fossils. As well as being an effective reagent for the removal of pyrite oxidation products, without endangering calcareous structures, it is safer and easier to use than previous techniques. It can also be readily adapted to suit the requirements of individual specimens.

Supplier of ethanolamine thioglycollate. Robinson Brothers Limited, Phoenix Street, West Bromwich, West Midlands B70 0AH



TEXT-FIG. 1. Dimorphophoplitid ammonite from the Gault Clay (Albian, lower Cretaceous; Folkstone, Kent) preserved in pyrite. A, before treatment, showing typical areas of pyrite oxidation speckled white. B, after removal of pyrite oxidation products with ethanolamine thioglycollate.

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